Radiolysis of HA in aqueous solutions using gamma rays

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Abstract The present work investigated the radiolysis of HA (Humic acids) in aqueous solutions and under gamma radiation. Absorbances at the range of 200–800 nm and chemical oxygen demand (*COD*) were used to characterize the degree of degradation of HA. The results indicated that absorbances and the concentrations of *COD* were decreased with increasing of irradiation dose while with increasing of irradiation dose the pH of the solutions was decreased at first and then increase. In addition, the effects of initial pH and primary solution concentrations on HA degradation were also investigated. It is shown that the higher primary solution concentrations, the lower degradation efficiency under the same irradiation dose. And the degradation efficiency of HA under neutral conditions is better than in acidic or alkaline conditions.

Key words Radiolysis, Gamma rays, HA

1 Introduction

Humic acids (HA) is a kind of Macromolecular organic matter in natural water, contains many kind of functional group, such as hydroxyl group, carboxyl group, benzo- quinonyl, methoxy group, and carbonyl group[1]. During chloridizing disinfection of drinking water, it can reacts with Cl_2 to form chlorinated disinfection by-produces(DBPs), such as THMs[2], and can affect water's color and taste. As HA can collect some trace metal elements[3] it can reduce water's mineralization even increased some of heavy metal's toxicity. So, it is very important to remove (or reduce concentration of) HA from water.

HA is a bio-refractory material. In the research of using activated sludge to degrade HA[4], X.Y. Xiong found its biodegradability is very poor and degradation rate is very slow. Traditional methods of its degradation include coagulation sedimentation[5], adsorption[6], ion exchange[7] technique and so on. In recent years, some advanced oxidation processes (AOPs) such as Fenton[8], photocatalytic oxidation[9], ultrasound oxidation[10], and electrochemical oxidization[11] have been used in the study of HA degradation. Ionization radiation technology is an efficient, rapid and advanced oxidation technology, without second pollution, have been widely used in the exploration of organic pollutant degradation and waste water treatment[12]. However, using ionization radiation to do the HA degradation research is few and far between. Hidehiko Arai *et al.* had degraded HA by using ionization radiation and ozonation, which have studied the chlorination products and the chain reaction mechanism during the oxidation of HA[13]. H.B. Liang *et al.* have used electron beam to degrade HA, dealing with the difference of chemical structure and biological activity before and after irradiation[14].

This paper aimed to study the degradation effect of gamma irradiation to HA in aqueous solutions. Its degradation is shown by measuring the change of UV-Vis absorbance, *COD* and pH value before and after irradiation. Furthermore, the factors, such as pH value, and initial concentrations of HA, affected on degradation were investigated.

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2 Materials and methods

2.1 Materials

The HA (BR) used in the present study was purchased from Shanghai Fanke biotech company (Shanghai, China), and both of the sodium hydroxide (AR) and sulfuric acid (AR) were obtained from Nanjing Reagent (Nanjing, China). All aqueous solutions were prepared with ultrapure water obtained from an UP-10 ultrapure water system (NJQY, Nanjing, China), resulting in a resistivity >18.2 MΩcm.

2.2 Analysis methods

The pH of the solutions was measured by PHS-3C pH meter, Chemical Oxygen Demand (*COD*) was analyzed using the *COD* Meter (ET99718, Italy), UV-Vis absorbance was determined by UV-1800 (Shimadzu, Japan).

2.3 Experimental procedure

The desired concentrations of HA solutions were prepared between 0.02 g/L to 0.12 g/L by using ultrapure water. The pH of the solution was adjusted by H_2SO_4 (1 mol/L) or NaOH (1 mol/L). Each sample of 50 mL was sealed in the 100 mL brown glass bottle with plastic cap. Each of the concentrations of HA solutions were prepared two samples, one of the sample were irradiated under the gamma radiation (^{60}Co, 1 kGy/h, NUAA), the range of irradiated dose between 0 to 40 kGy, and the dose were determined by Silver dichromate dose meter. The other preservation was done in the shadows as a blank sample. All of the samples were analyzed at the same time after irradiation. All operations were performed at room temperature.

3 Results and discussion

3.1 Effect of irradiation dose on UV-Vis absorption spectrum

To clarify the degradation characteristics of HA as a result of gamma irradiation, spectroscopic data for the irradiated and un-irradiated HA were compared. Fig.1 shows the UV-Vis absorption spectrum of HA which the concentration was 0.12 g/L and the range of absorbance between 190 to 800 nm with a maximum absorption peak at 310 nm. There are strong absorbance at 250–400 nm, it may be due to that HA's composition is very complex and contains a large number of benzene rings and have a large conjugated system in HA molecule[15]. The absorbance at 200–500 nm decreased with increasing the irradiation dose as a result of gamma irradiation. It was confirmed that HA was effectively decomposed under gamma irradiation. However, the absorbance at 500–800 nm was slowly increasing at the beginning of the irradiation, and then decreased with increasing the irradiation dose. This would be due to some intermediates formed in the process of HA decomposition at the beginning of irradiation, and then they were decomposed with increasing irradiation dose.

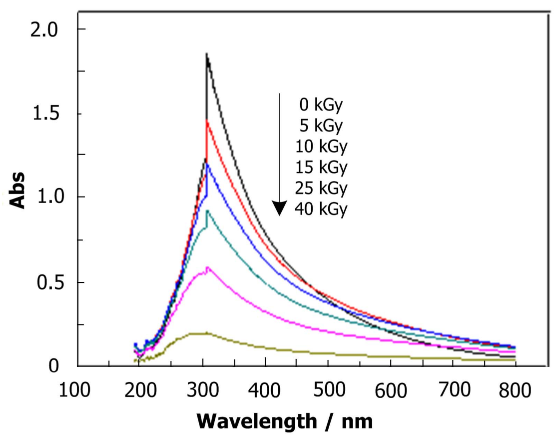

Fig.1 UV-Vis absorption spectra of HA solutions.

3.2 Effect of irradiation dose on *COD* removal

The *COD* removal was used to represent the degree of HA degradation by gamma radiation. The *COD* removal was calculated as follow.

$$COD\text{removal}(\%) = \frac{COD_0 - COD_D}{COD_0} \times 100 \qquad (1)$$

where COD_0 and COD_D were the *COD* concentrations before and after gamma irradiation.

Figure 2 shows the effect of irradiation dose on *COD* removal when initial concentration is 0.12 g/L. It can be seen that the *COD* removal of HA solutions increased with increasing the irradiation dose. The *COD* removal was up to 52% when the irradiation dose reaches 40 kGy. This suggests that the degradation of the HA solution by gamma irradiation is effective.

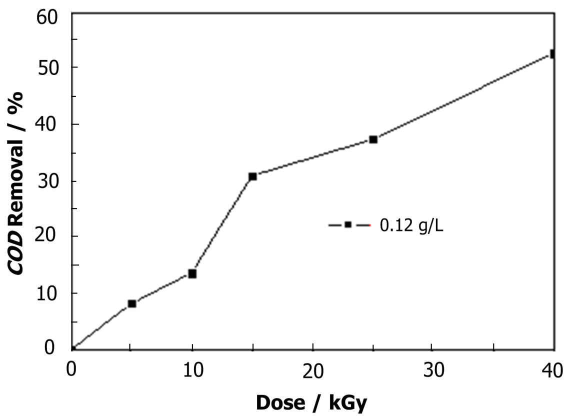

Fig.2 Effect of irradiation dose on *COD* removal of HA solutions.

3.3 Change of pH

The effect of irradiation dose on pH was investigated at initial concentration of 0.12 g/L. As shown in Fig.3, the initial pH of HA solution was 7.05. After irradiation, the HA solutions pH decreased with increasing irradiation dose. It's because some small molecule organic acids such as oxalic acid, formic acid generated in the process of HA decomposition[16]. However, when the irradiation dose was up to 40 kGy, the solutions pH showed small increase, which might be due to the small molecule acids resulted from completely mineralized of HA to form CO_2 and H_2O under the high irradiation dose condition.

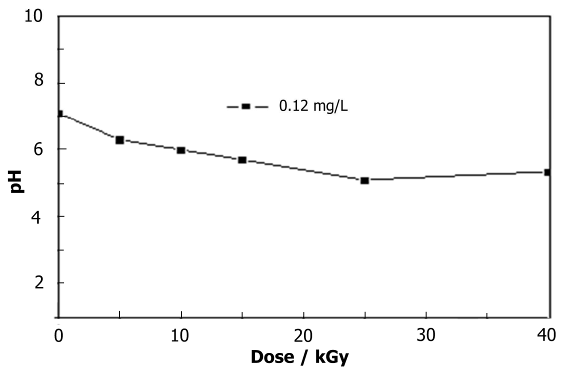

Fig.3 Effect of irradiation dose on HA solution's pH.

3.4 Effect of initial concentrations on *COD* removal

Figure 4 shows the *COD* removal of different concentrations of HA solutions after gamma irradiation with different irradiation doses. It should be noted that the HA solutions initial pH was 7.05 with different concentration of HA, 0.02 g/L, 0.04 g/L, 0.08 g/L, 0.12 g/L respectively. As show in Fig.5, it is clearly that the initial concentration acts an important role in the process of HA decomposition. It can be seen that the *COD* removal decreased with increasing initial concentrations under the same irradiation dose. For example, for the same gamma irradiation dose (15 kGy), the HA solution's *COD* removal is 95% when the initial concentrations was 0.02 g/L. However, the *COD* removal is only 31% when the initial concentration was 0.12 g/L. It means that the amount of organic carbon with higher HA concentration is larger than that of low concentration and the OH radical formed in this process is dependent on the irradiation doses, so the HA degradation efficiency should be low with its high concentration[17].

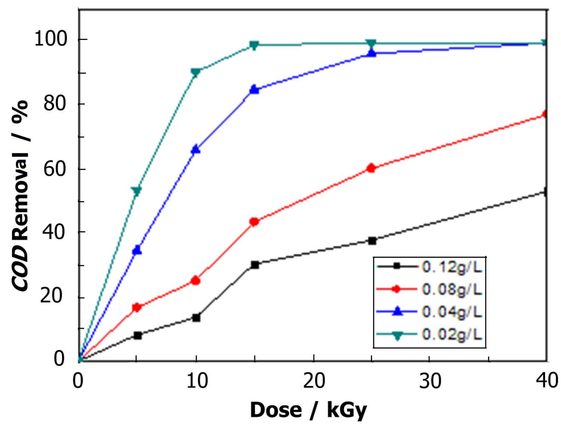

Fig.4 Effect of initial concentrations on *COD* removal.

3.5 Kinetic analysis of *COD* removal

As illustrated in Fig.4, approximately *COD* removal of HA solution exponentially ascends with the increase of irradiation dose, indicating that *COD* removal of HA solution maybe follow pseudo first-order kinetics. By assuming that the gamma irradiation process of HA follows pseudo first-order kinetics, relationship between *COD* removal of HA solution with irradiation time would be follow Eq.(2).

$$\ln\left(\frac{C_t}{C_0}\right) = -kt \tag{2}$$

C_0 and C_t were the *COD* values before and after irradiation, t was the irradiation time (h), k was the reaction rate constant.

As shown in Table 1, the high value of correlation coefficient R in Table 1 suggests that the

degradation of HA solution by gamma radiation follows pseudo first-order kinetics. It can be seen that the k value decreases with the increment of initial HA solutions concentration. As discussed above, under the same irradiation condition and pH value, when the HA concentration was lower, the relative probability that HA reacting with OH radical was greater.

Table 1 Degradation kinetics for HA solutions on difference initial concentrations

Concentrations (g/L)	Kinetics equations	Correlation coefficient (R^2)
0.12	$\ln C_t/C_0 = -0.0194t + 9.2607\times10^{-4}$	0.9727
0.08	$\ln C_t/C_0 = -0.3683t + 0.0149$	0.9951
0.04	$\ln C_t/C_0 = -0.0863t - 0.0658$	0.9936
0.02	$\ln C_t/C_0 = -0.2387t + 0.1257$	0.9823

3.6 Effect of initial pH on *COD* removal

For investigating the effect of initial pH on the degradation efficiency, the experiment was performed at initial HA concentrations of 0.1 g/L and irradiation dose was 25 kGy, and pH was changed from 3 to 12 as shown in Fig.6. The *COD* removal was different with the different initial pH values. It is clear that the optimal *COD* removal condition was pH 3. Accordingly, the pH may affect the molecular structure of HA, which will result in different degradation efficiency. On other hand the oxidation potential of OH radical at low pH is higher than that at high pH, so the degradation of HA may be favorable to OH at low pH.

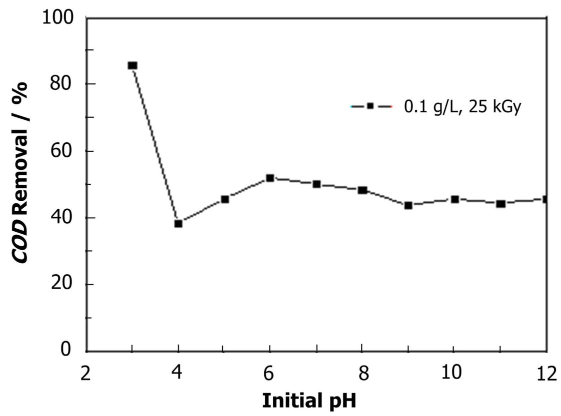

Fig.5 Effect of initial pH on *COD* removal.

4 Conclusion

The degradation of HA in aqueous solution was investigated by gamma irradiation. Results from this study show that gamma irradiation might be effective method for degradation of HA in aqueous solution. After irradiation, UV-Vis absorbance and *COD* concentration of the HA solution have a significant decline. If initial concentration is 0.12 g/L, initial PH=7, after 40 kGy irradiation, UV-Vis absorbance at 310nm will decline 90%, *COD* concentrations will decline 52%. Further, the change of *COD* concentration matched the first-order kinetics equation. The higher the initial concentration is, the lower the reaction rate coefficient is.

In addition, initial concentration and initial pH of HA solutions have important effects on irradiation degradation. Under the same irradiation condition, the efficiency of irradiation degradation decreases with increase of initial concentration. When initial pH value is between 6 and 8, the efficiency of the irradiation degradation is the highest. Too low or too high initial pH value is not conducive to the irradiation degradation of HA solutions.

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